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The purpose of this work has been to investigate laser multiphoton ionization (MPI) as an atmospheric pressure ionization source for ion mobility spectrometry (IMS). This has included a study of the potential of MPI for improving selectivity and specificity in IMS and also an investigation of the fundamentals of laser MPI under atmospheric conditions. A second focus of this work has been to extend IMS to nonvolatile molecules using a pulsed laser desorption method for volatilization. The final report contains the research findings.

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**Ion Mobility Spectrometry With Laser-Produced Ions  
(Final Report)**

**David M. Lubman**

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**U.S. Army Research Office**

**Grant #DAAG 29-85-K-0105**

**The University of Michigan  
Department of Chemistry  
Ann Arbor, MI 48109**

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## A. Statement of Problem

The purpose of this work has been to investigate laser multiphoton ionization (MPI) as an atmospheric pressure ionization source for ion mobility spectrometry (IMS). This has included a study of the potential of MPI for improving selectivity and specificity in IMS and also an investigation of the fundamentals of laser MPI under atmospheric conditions. A second focus of this work has been to extend IMS to nonvolatile molecules using a pulsed laser desorption method for volatilization.

## B. Outline of Research Findings

During this granting period we have set-up an atmospheric pressure ionization mass spectrometer interfaced to our ion mobility spectrometer in order to mass analyze the ions produced in the IMS by laser ionization (see figure 1). This equipment was provided under the DOD Instrumentation Program under contract #DAAG-29-81-C-0023. The device was manufactured by PCP, Inc. (West Palm Beach, FL) and the vacuum station and associated electronics were built in-house. The device is operational and we have been studying laser ionization at atmospheric pressure in our IMS in order to compare the results to conventional  $^{63}\text{Ni}$   $\beta$  source ionization. Our results are reported in a manuscript entitled "Atmospheric Pressure Ionization with Laser-Produced Ions" of which the most important points are summarized herein.

We have explored laser ionization in an IMS under different drift gas environments. In every case we obtain one peak which when mass analyzed is found to be  $\text{M}^+$  or  $\text{MH}^+$  or  $\text{M-H}^+$ . In no case is fragmentation observed even under fairly high power at 266 nm (i.e. >30 MW) and the parent ion or its protonated counterpart are always observed for identification. Thus, laser ionization appears to be a tool for efficiently and softly ionizing molecules at atmospheric pressure. This was found to be true in not only pure  $\text{N}_2$  but also air, Ar,  $\text{CO}_2$  and P-10 gas. The IMS spectrum in each drift gas was generally found to be the same whether laser ionization or the  $\text{Ni}$   $\beta$  source was the means of ionization. There were several exceptions to this including aniline and triazine; however, upon mass analysis the same ions were detected. This difference in drift time is probably due to weak clusters that may form in the  $\text{Ni}$   $\beta$  reactor; however, these clusters fall apart upon injection into vacuum in a quadrupole mass spectrometer due to shock waves produced in the expansion. We also find that the drift time in  $\text{CO}_2$  is not a function of the mass of the ion. This is apparently due to clusters of the highly polarizable  $\text{CO}_2$  around an inner ionic organic core.

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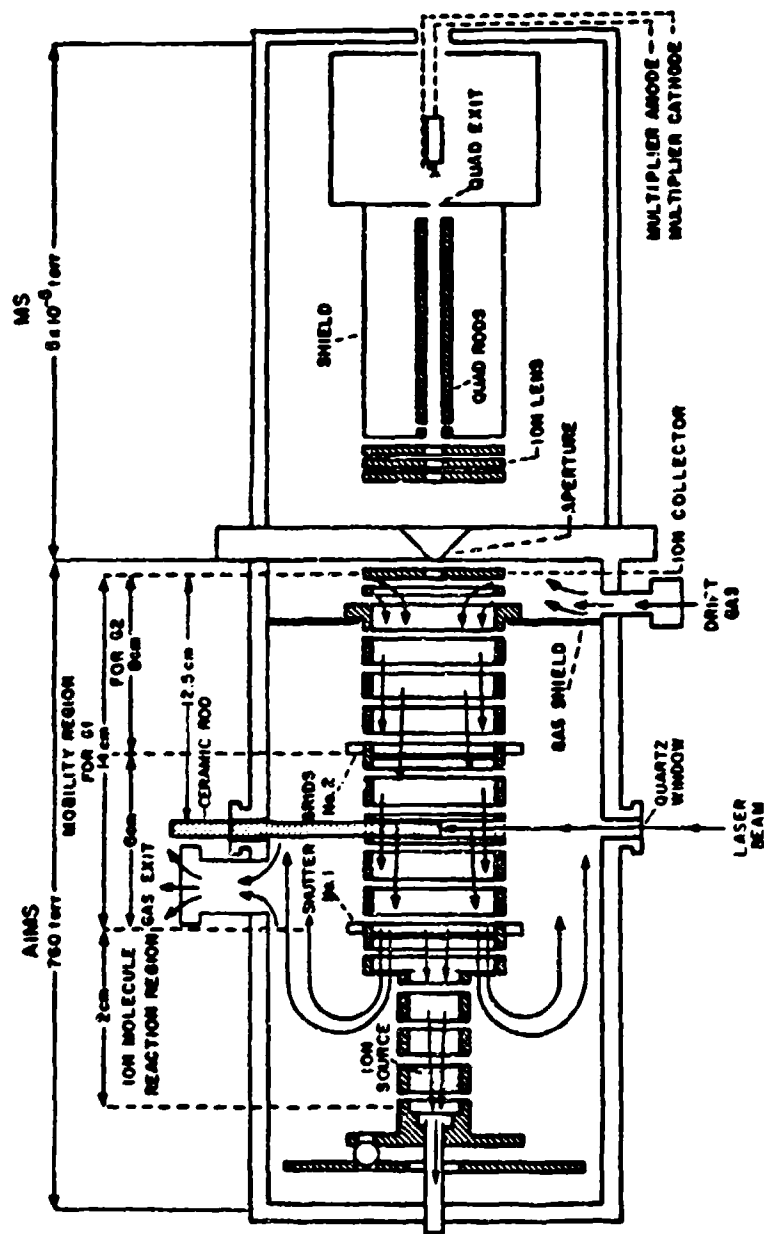


Figure 1. Schematic of the atmospheric pressure ionization mass spectrometer/ion mobility drift tube apparatus with laser desorption probe.

However, upon expansion into the mass spectrometer system we observe only  $M^+$  ( $MH^+$ ) probably due to shock waves that destroy the weakly bound clusters at 220°C. At 85°C, though, clusters of  $CO_2$  plus the molecular ion can be observed since the complex remains stable under these conditions. In addition, the IMS spectra  $K_0$  values were found to vary directly as,  $\alpha$ , the polarizability of the gas, except in the case of  $CO_2$  where large clusters are formed.

The addition of the mass spectrometer has allowed us to further evaluate some of the results of our earlier work. One such example is the change in  $K_0$  for pyridine as a function of temperature. This was shown to be due unambiguously to the formation of dimers even at very low concentration. We also investigated laser induced fragmentation at very high powers (>100 MW) and found that even under conditions where only  $C^+$  would be observed in a mass spectrometer under vacuum that at atmospheric pressure the smallest fragment observed is  $C_6H_7^+$ . Thus, laser ionization at atmospheric pressure may serve as a means of softly ionizing molecules that might otherwise undergo extensive fragmentation in the ionization process.

More recently, we have begun studying laser ionization in He buffer gas. In other cases such as 1 atm of  $N_2$ , air or Ar using R2PI at 266 nm we always observe either  $M^+$  and  $MH^+$  with no accompanying fragment peaks in our IMS as monitored by a mass spectrometer. He though has a fundamentally much smaller collisional effectiveness constant  $\epsilon$  and our initial results show that fragmentation can be induced. Using a heavier gas such as  $N_2$ , the excited ionic state collisionally relaxes at atmospheric pressure before fragmentation can proceed. Since the relaxation processes are not nearly as effective with the lighter He, some fragmentation occurs although not as extensively as observed under vacuum. The possibility now exists for using a combination of He and  $N_2$  at a specific laser input energy to control the formation of a specific ion fragment for identification. This would be extremely useful for distinguishing ions of similar mass and thus similar  $K_0$  value, but which may yield very different fragments in the IMS under the same conditions. This method could be used, for example, to distinguish TNT isomers. In present mass spec techniques such as tandem mass spectrometry the use of collisions with other gases serves as a nonspecific means of producing fragmentation. In this work, we plan to use atmospheric pressure collisions to effectively control fragmentation.

In preliminary results using an in-house constructed IMS device, the gas mixture was varied from pure  $N_2$  to a mixture of 80% He/20%  $N_2$ . Using laser ionization at 266 nm, only one peak was observed in pure  $N_2$ . As the percentage of He was

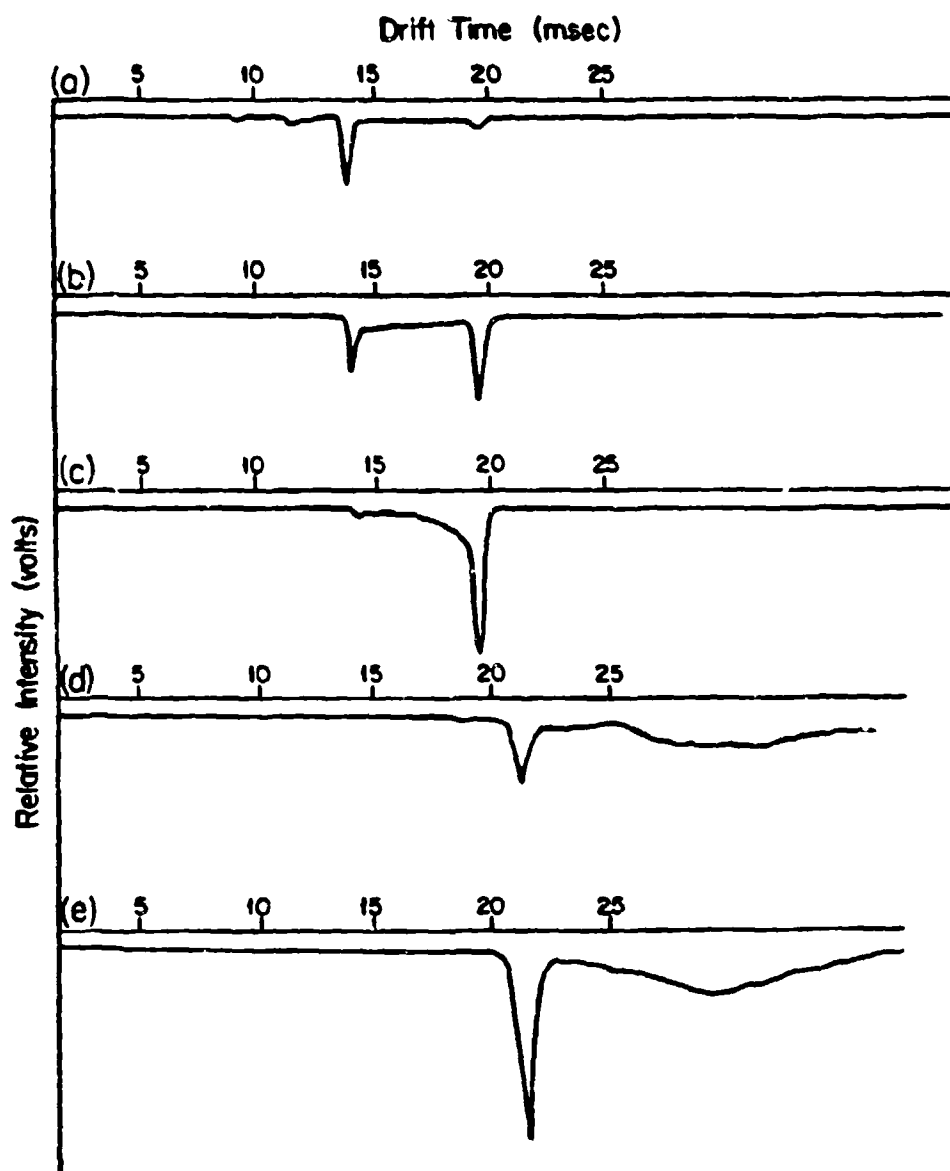


Figure 2. Ion mobility spectrum for DMMP at 220 °C in N<sub>2</sub> at a concentration of (a) 15 ppb, (b) 50 ppb, and (c) 100 ppb for ions produced by the <sup>63</sup>Ni B source and (d) 15 ppb and (e) 100 ppb for ions produced by laser radiation at 266 nm.

increased, additional peaks were observed which may be due to an enhanced ability to produce fragmentation. In order to study this further, a small atmospheric pressure ion cell has been constructed which is interfaced to our mass spectrometer system. Lower voltage fields are used here in order to prevent arcing which readily occurs in helium gas. Experiments in this system are now in progress.

In other work, we have studied the ionization of DMMP in an ion mobility spectrometer. We have found that laser ionization at 266 nm can induce efficient direct ionization of DMMP to produce  $M^+$  as detected in the mass spectrometer (See figure 2). Although the ionization potential of DMMP is estimated to be 10.4 eV there is sufficient hot-band population to allow efficient ionization. We have also found that dimerization occurs at very low concentration levels for DMMP and by 100 ppb mainly the dimer is detected in the mass spectrometer. More recently we have begun to explore laser ionization of other related chemical warfare agent analogs.

This work has been supported by ARO Grant DAAG 29-85-K-1005. The personnel directly responsible for this work are Professor David M. Lubman, P.I. and Mr. Leonidas Kolaitis, who recently received his Ph.D. M. Tierney and C. H. Sin have also participated in this project part-time.

2. A second project which has been pursued is the detection and analysis of nonvolatile and thermally labile compounds using laser desorption in atmospheric pressure mass spectrometry. This may be of particular interest to DOD because it allows the extension of IMS/MS to pharmaceutical and biological molecules and thus the ability to detect biological toxins with great sensitivity. Many biological compounds such as N-heterocyclic based drugs and amino acids and peptides are nonvolatile and thermally labile so that if heated they decompose before sufficient vapor pressure is produced for detection. We therefore use rapid laser desorption of these materials from a surface into the gas phase at atmospheric pressure in pure  $N_2$  (see figure 3). The ion-molecule reagents generated by a  $Ni^{2+}$  source are then used to softly ionize these biological species and the product ions are focused into the API mass spectrometer. This method has proved to be an incredibly sensitive means of detecting these compounds where sensitivity limits probably lie in the sub-ppb region. This sensitivity appears to be due to the very efficient laser desorption process which vaporizes all the material on the surface in several laser pulses and the chemical ionization-API method which ionizes 100% of the molecules in the reaction region due to the large number of collisions at atmospheric pressure. This method is particularly effective for molecules with high proton

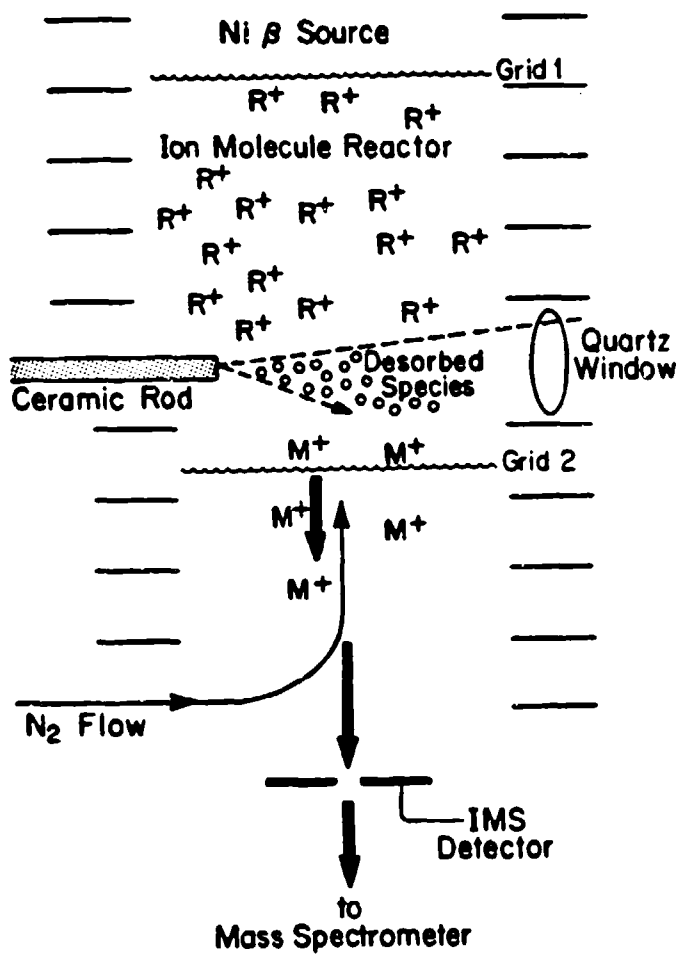


Figure 3. Laser desorption in IMS/MS setup. Desorption probe is inserted directly into the drift region.

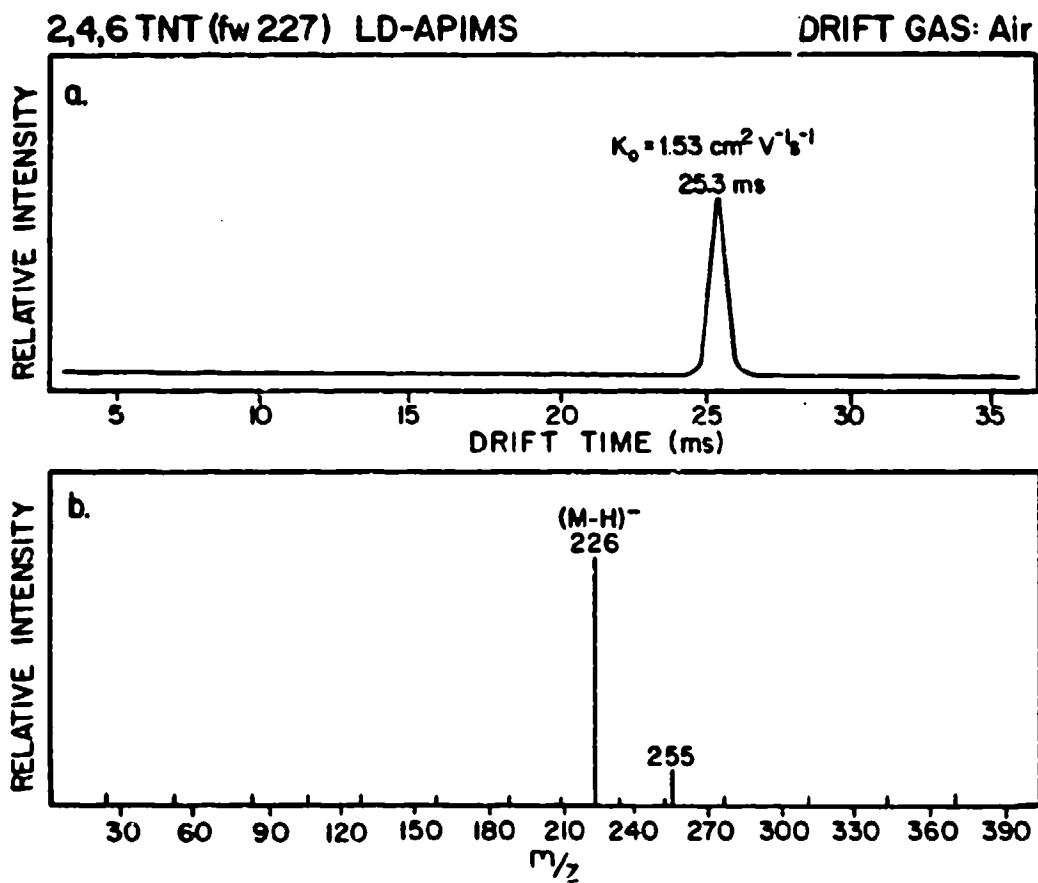


Figure 4. Laser desorption at 50 °C in (a) IMS of military grade TNT in negative mode and (b) IMS/MS of same sample in negative mode.

affinities which includes large classes of biological species such as N- and S- heterocycles. The laser desorption generally appears to produce gas phase species intact before decomposition can occur and the chemical ionization API is a soft ionization tool so that generally molecular ions are produced with little or no fragmentation for exact identification in the mass spectrometer.

Although laser desorption can produce direct ionization from the surface at the power levels used in this experiment, i.e.  $10^7$  W/cm<sup>2</sup>, 99% of the species desorbed into the gas phase should be neutrals. We have used this method to detect nonvolatile molecules such as amino acids, purine and pyrimidine bases and their phosphate sugars, and various antidepressant drugs and catecholamines. The ability to detect such compounds with great sensitivity and with unique identification by mass spectrometry may have important ramifications for quality control in the pharmaceutical industry and in clinical analysis. This technique could be interfaced with liquid chromatography separation where the eluent is placed on a moving belt, the solvent evaporated and then desorbed into the APIMS system. In addition, this method may be useful for determining contamination on surfaces for compounds such as chemical and biological agents.

Other work using this method involves the detection of explosive materials using LD in atmospheric pressure. We have examined compounds such as 2,4 and 2,6 DNT, 2,4,6 TNT (see figure 4), RDX (see figure 5), HMX, nitroglycerin, PETN, Composition B, LX-14 and C-4. Detection has been investigated using both positive and negative modes although the negative mode appears to be more sensitive. The ion mobility spectrometer with mass analyzed results has served as the means of identification. In each case we find soft desorption-ionization of the molecules with molecular ions or simple rearrangement products being detected in the negative mode. In both the negative and positive mode the ion products obtained appear to change as a function of gas temperature with adduct ions with -NO and -NO<sub>2</sub> appearing or loss of -H<sub>2</sub>O, -NO, -HNO<sub>3</sub> or -NO<sub>2</sub> occurring in the mass spectra. In any case, though, the spectra obtained are generally very simple with only one or two major peaks. The results obtained are consistent with those ions observed in chemical ionization (CI) conditions under vacuum; however, the API spectral pattern is generally much simpler. Electron beam ionization of these compounds generally provides extensive fragmentation and often only low mass ions are the major peaks in the spectrum. Our results are also comparable to Spangler's IMS and MS data on DNT and TNT although some differences are apparent.

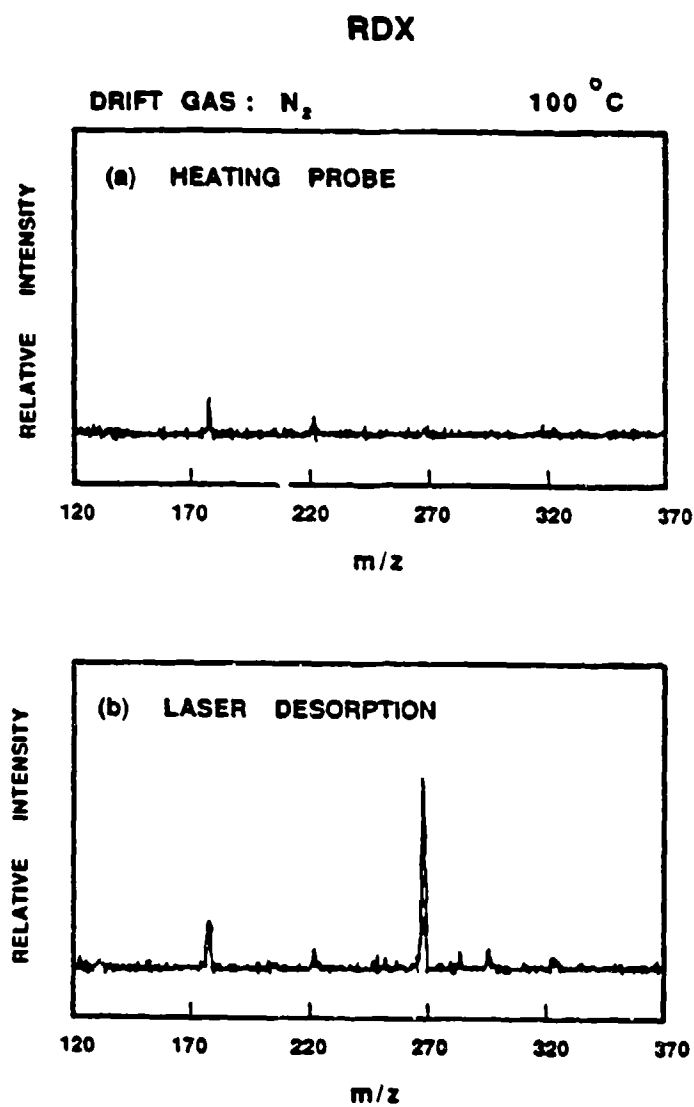
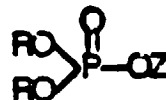


Figure 5. IMS/MS of RDX at 100 °C obtained by  
(a) heating of probe and (b) laser desorption in N<sub>2</sub>.

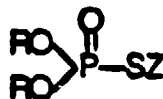
The laser desorption technique provides rapid vaporization without decomposition of the explosive materials studied here. Detection below 0.1 ng is obtained in the negative mode and is limited by our ion collection efficiency. This method can also provide simultaneous vaporization of mixtures such as C-4 (plasticizer + RDX) and composition B (TNT + RDX) whereas slow heating may provide a distorted abundance of one compound. In addition, we have been able to study real samples mixed with plasticizers such as LX-14(HMX) and Det-Cord (PETN). We have also compared the desorption method to a direct probe arrangement where the sample is placed on the end of a ceramic probe and heated by the hot bath gas (see figure 3). This heating arrangement works quite well in some cases although the sensitivity will be limited by the slow rate of vaporization at 60 °C and any pyrolysis on the surface.

We are presently studying the LD and direct probe methods for detection of chlorinated and phosphoroorganic pesticides that are analogs to neurotoxins and chemical warfare agents. We have studied four such basic structural groups including:

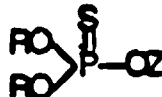
1. Phosphates



2. Phosphorothiolates



3. Phosphorothionates



4. Phosphorodithioates



5. Miscellaneous

where R is usually a small aliphatic group and Z is often an aromatic or heterocyclic ring or small aliphatic side chain.

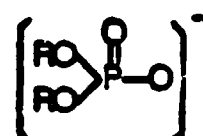
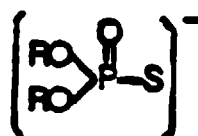
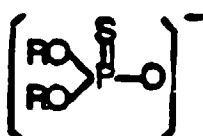
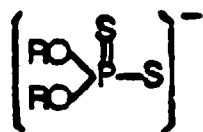
Our results demonstrate that the LD-APIMS mass spectra of most OPs studied so far exhibit several general features:

(1) In most cases positive LD-APIMS mass spectra exhibit the  $(M+H)^+$  ion as the base peak with high intensity.

(2) In most cases, negative LD-APIMS mass spectra exhibit the phosphorus ester group specific ion  $(M-Z)^-$  as the base peak.

(3) The order of the tendency to form the specific ion  $(M-Z)^-$  is:

Class 4 > Class 3 > Class 2 > Class 1



R-CH<sub>3</sub>: m/z=157

m/z=141

m/z=141

m/z=125

R-C<sub>2</sub>H<sub>5</sub>: m/z=185

m/z=169

m/z=169

m/z=153

(4) For some OPs which contain a chlorinated Z moiety, the  $(M-Z+Cl)^-$  ion appears as the base peak, though the specific ion  $(M-Z)^-$  also appears with strong intensity.

(5) For some compounds, such as Demeton mixed isomer in class 2 and Phorate in class 4,  $(M+Z)^+$  is observed as the base peak in the positive mode, and  $(M-R)^-$  is observed as the second most intense peak in the negative mode.

(6) For the Parathion group (with  $Z = C_6H_5NO_2$ ) in class 3 the phenolate ion  $(OC_6H_5NO_2)^-$  is observed as the base peak, though other investigators using CI have found the thiophenolate ion  $(SC_6H_5NO_2)^-$  to be the base peak.

(7) In some compounds, such as Carbophenothion in class 4, the Z moiety contains thiophenolate  $SC_6H_5Cl$  and the  $(SC_6H_5Cl)^-$  ion is observed as the base peak in the negative mode while the  $(M-SC_6H_5Cl)^+$  ion is observed as the base peak in the positive mode.

(8) In most cases, the results of using an In-beam heating probe are similar to LD-APIMS, however, the LD-APIMS experiments can be performed at a lower temperature which appears to prevent decomposition. The LD-APIMS results show enhanced formation of the specific fragments discussed above without extra fragments observed when using the heating probe method due to thermal decomposition.

(9) We have begun interfacing the LD/APIMS method to laser R2PI at 266 nm for detection of some of the OP compounds with an absorbing aromatic center. Since the different OP compounds have absorption maxima that are shifted from one another we will examine the selectivity possible in the IMS by varying the laser ionization wavelengths. A wavelength  $\sim 220$  nm will be used to ionize some of the nonaromatic OP compounds.

### C. Publications

Supported by ARO Grant DAAG29-85-K-1005.

1. L. Kolaitis and D. M. Lubman, "Atmospheric Pressure Ionization Mass Spectrometry With Laser-Produced Ions", Anal. Chem. 1986, 58, 1993.
2. L. Kolaitis and D. M. Lubman, "Detection of Nonvolatile Species by Laser Desorption Atmospheric Pressure Mass Spectrometry", Anal. Chem. 1986, 58, 2137.
3. D. M. Lubman and S. D. Huang, "Detection of Explosives Using Laser Desorption in Atmospheric Pressure Mass Spectrometry", Proceedings of the 1986 Scientific Conference on Chemical Defense Research, ed. by M. P. Rausa, November 1986.
4. S. D. Huang, L. Kolaitis and D. M. Lubman, "Detection of Explosives Using Laser Desorption in Ion Mobility

Spectrometry/Mass Spectrometry", Applied Spectroscopy 1987, 41, 1371.

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5. R. Tembreull, C. H. Sin, H. M. Pang and D. M. Lubman, "Laser Ionization Mass Spectrometry in Supersonic Beams", Optics News, 1986, 12, 16.
6. M. Tierney and D. M. Lubman, "Laser-Induced Photoconductivity in Thin Organic Films", Appl. Spec., 1987, 41, 880.
7. D. M. Lubman, "Multiphoton Ionization Mass Spectrometry", Progress in Analytical Spectroscopy 1987, 10, 529.
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9. H. M. Pang, C. H. Sin, D. M. Lubman and J. Zorn, "Design of a Pulsed Source for Supercritical Fluid Injection Into Supersonic Beam Mass Spectrometry", Anal. Chem. 1986, 58, 1581.
10. C. H. Sin, H. M. Pang, D. M. Lubman and J. Zorn, "Supercritical Carbon Dioxide Injection in Supersonic Beam Mass Spectrometry", Anal. Chem. 1986, 58, 487.

**D. Personnel and Degrees****Supported by ARO**

1. Leonidas Kolaitis, Ph.D. 4/88
2. S. D. Huang, M.A. 12/87

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3. C. H. Sin, Ph.D. 10/87
  4. Michael Tierney, Ph.D., 8/88
- 
1. Ph.D. Thesis-Leonidas Kolaitis, "Laser Ionization/Desorption-Mass Spectrometry", in press. Joint Thesis, University of Michigan and University of Antwerp, February 1988.
  2. Ph.D. Thesis-Chung Hang (Joseph) Sin, "Resonant Two-Photon Ionization and High Pressure Fluid Injection in Supersonic Beam/Mass Spectrometry", University of Michigan Department of Chemistry, October 1987.
  3. Ph.D. Thesis-Michael Tierney, "Laser Induced Photoconductivity in Thin Organic Films", University of Michigan, Department of Chemistry, October 1988.